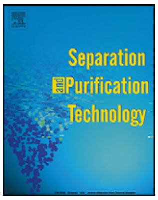
Separation and Purification Technology 71 (2010) 63–69

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Facilitated transport of uranium(VI) across a bulk liquid membrane containing thenoyltrifluoroacetone in the presence of crown ethers as synergistic agents

Mojtaba Shamsipur[a,*], Reza Davarkhah[b], Ali Reza Khanchi[c]

[a] Department of Chemistry, Razi University, Kermanshah, Iran
[b] Department of Chemistry, Tarbiat Modares University, Tehran, Iran
[c] Chemistry Research Department, School of Nuclear Science Research, Nuclear Science and Technology Research Institute, Tehran, Iran

ARTICLE INFO

Article history:
Received 23 July 2009
Received in revised form 30 October 2009
Accepted 2 November 2009

Keywords:
Bulk liquid membrane
Uranyl ion
Uphill transport
Thenoyltrifluroacetone
Crown ether

ABSTRACT

A study has been made on carrier-mediated transport of uranium(VI) using a bulk liquid membrane prepared by dissolving equimolar amounts of thenoyltrifluoroacetone (HTTA) and dicyclohexyl-18-crown-6 (DC18C6), as a synergistic agent, in chloroform. The source phase comprised of a solution of UO_2^{2+} in water at pH 2.0, and a solution of 0.2 M hydrochloric acid and 4.0×10^{-3} M sodium dodecylsulfate (SDS) served as the receiving phase. While in the presence of 0.02 M HTTA in the membrane phase only 19% of uranyl ion could be transported into the receiving phase, after several hours, the addition of 0.02 M DC18C6, as a suitable synergistic agent, into the membrane phase resulted in the quantitative transport of uranyl ion in 9 h. Various factors influencing the transport process such as the pH of source and receiving phases, the types and concentration of surfactant and carriers concentrations were optimized. The transport efficiency of uranyl ion using different crown ethers followed the order: DC18C6 > DB18C6 > DB24C8 > DB21C7 > DB15C5. Meanwhile, the addition of SDS as a cationic surfactant in acidic receiving phase solution, under optimum conditions, significantly lowered the concentration of acid required and increased the transport efficiency. A kinetic model was also used to describe the U(VI) transport behavior, assuming that it obeys the kinetic laws of two consecutive irreversible first-order processes. The interference from different transition metal ions was found to be negligible. The interference from Th^{4+} and Cu^{2+} could be eliminated by using EDTA as a proper masking agent in the source phase.

1. Introduction

The use of various types of liquid membranes for separation processes has attracted an increasing attention in recent years [1–3]. Membrane technology has been widely utilized for carrier facilitated metal ion separations [4–13] and, to a lesser extent, for separation of organic substances [14–16]. The principle of such separation techniques was described by Danesi et al. [4]. An important advantage for this technique is that, in the liquid membrane technology, the extraction, stripping and regeneration operations are combined in one single step. Also the organic membranes are short-term mediators only, and their extraction capacity is of no essential significance. As a result, a great variety of insoluble, inert and harmless organic liquids can be used as an intermediate liquid, containing only a small amount of carriers. Thus, very expensive, highly selective, tailor-made carriers can also be used economically [3].

The phenomenon known as synergism has been extensively studied from both theoretical and practical points of view in the last decade [17]. Various combinations of extractants responsible for synergism have been described in books and reviews [18,19]. Bond et al. have presented a comprehensive review on synergism phenomena using crown ether-containing systems [20]. Combinations of a β-diketonate and various crown ethers as neutral adducts, which provide synergism, have been frequently employed in the liquid–liquid solvent extraction of actinides [21,22]. However, there are few reports where actinides have been transported across a bulk liquid membrane containing a mixture of crown ethers and β-diketones [9].

To provide a basis for more complete evaluation of such synergistic systems in transport experiments, in this work, we studied the carrier-mediated transport of uranyl ions by mixtures of thenoyltrifluoroacetone (HTTA) and a series of crown ethers (CEs) in a bulk liquid membrane (BLM). Thus, effect of various experimental parameters, which may influence the transport behavior of uranium, viz. nature of diluent, carrier concentrations, feed acidity, the type and concentration of the acid used as stripping agent in the receiving phase and the type and concentration of surfactant in the

---

[*] Corresponding author. Tel.: +98 21 66908032; fax: +98 21 66908030.
E-mail address: mshamsipur@yahoo.com (M. Shamsipur).

1383-5866/$ – see front matter
doi:10.1016/j.seppur.2009.11.003

latter phase has been investigated. The carrier activity of HTTA–CEs toward the selective transport of uranium in the presence of thorium and some other interfering ions has also been studied.

2. Experimental

2.1. Reagents

Thenoyltrifluoroacetone (HTTA) and Complexone III (EDTA, disodium salt) were obtained from Fluka and used without further purification. The crown ethers dibenzo-15-crown-5 (DB15C), dicyclohexyl-18-crown-6 (DC18C6), dibenzo-18-crown-6 (DB18C6), dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8) and all surfactants from Aldrich were used as received. Carbon tetrachloride, dichloromethane, chloroform, 1,2-dichloroethane and the acids used were purchased from Merck chemical company and used as received. A stock solution of 0.01 M uranium(VI) was prepared from $UO_2(NO_3)_2{\cdot}6H_2O$ (Merck). Th^{4+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+} solutions were prepared from the corresponding reagent grade nitrate salts (Merck or Fluka). Doubly distilled water was used throughout.

2.2. Apparatus

The measurements were performed with a simultaneous inductively coupled plasma optical emission spectrometer (ICP-AES, Varian Vista-Pro, Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device (CCD). The ICP conditions are shown in Table 1. The pH of solutions was measured using a model 620 Metrohm pH meter with a combined glass–calomel electrode.

2.3. Procedure

All transport experiments were carried out at the ambient temperature of 23 ± 1 °C. A cylindrical glass cell (inside diameter 4.0 cm) holding a glass tube (inside diameter 2.0 cm), thus separating the two source and receiving aqueous phases was used [6]. The inner aqueous phase (source phase) contained U(VI) or a binary mixture of metal ions at a fixed pH of 2.0 (5 mL). The outer aqueous phase (receiving phase) contained a solution of 0.2 M hydrochloric acid and 4.0×10^{-3} M sodium dodecylsulfate (SDS) (10 mL). The chloroform membrane phase (20 mL) containing 0.02 M of each HTTA and DC18C6 laid below these aqueous phases, and bridged them. The organic layer was magnetically stirred by a Teflon-coated magnetic bar (3 cm × 5 mm diameter). Samples of both aqueous phases were analyzed for metal content by inductively coupled plasma-atomic emission spectrometry (ICP-AES). A similar transport experiment was carried out in the absence of the carrier for reference. Detailed conditions of experiments carried out in order to obtain optimal conditions are included in tables and figures.

Table 1
Instrumental and operating conditions ICP-AES measurements.

Parameter	Type or amount
Frequency generator (MHz)	40
Plasma viewing mode	Radial
Viewing height (mm)	8
Injector i.d. (mm)	2.5
Optical mount	Echelle grating + cross-dispersion
Grating line number (mm^{-1})	95
Focal length (cm)	40
Detector	CCD
Nebulizer	Concentric
Spray chamber	Cyclonic
RF power (kW)	1.2
Plasma gas flow rate ($l\,m^{-1}$)	13.5
Auxilary gas flow rate ($l\,m^{-1}$)	0.75
Nebulizer pressure (kPa)	200
Rinse time (s)	10
Selected emission line (nm)	U (367.007)

The reproducibility of the above system was investigated by accomplishing five replicate transport experiments. The percent of metal ion transport after 9 h was 99.1 ± 0.6%.

2.4. Liquid–liquid distribution coefficient measurements

The aqueous phase containing 1.0×10^{-4} M UO_2^{2+} at pH 2 was equilibrated separately with an equal volume of CCl_4 phase containing 0.05 M HTTA and then with that containing an equimolar mixture (i.e., 0.05 M) of HTTA + DC18C6 at room temperature. After 9 h agitation of the two mixtures, suitable aliquots of the aqueous phases were withdrawn for the assay of remaining UO_2^{2+} ion. The concentrations of the uranyl ion in the respective organic phases were then obtained by material balance. These concentrations were used to obtain the distribution ratios, D, in the absence and presence of DC18C6 in the HTTA containing organic phase.

3. Results and discussion

3.1. Preliminary studies

In a recent communication [13], we have reported the selective transport of U(VI) by benzoyltrifluoroacetone (HBTA), in which we found that the selective transport of U(VI) was conducted at pH 6 and in the presence of a suitable masking agent, trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (DCTA), to eliminate the interference effects of Th(IV) and several transition metal ions. To create a better selectivity for uranyl ion transport, possibly without using a masking agent, in this work, we were interested to examine the use of another β-diketone (i.e., HTTA) in combination with a macrocyclic crown ether, as a synergistic agent. It is interesting to note that, in a previously published work [9], Ramkumar et al. have also reported the transport of uranyl ion across a bulk liquid membrane using calixarenes and synergistic agents 18C6 or TOPO as carriers. However, it is to be noted that, in comparison with HTTA, the calixarenes as extractants are much difficult to synthesize and their production cost is very high. Instead, HTTA could be used as an efficient carrier in membrane systems so that the recovery and pre-concentration of the uranyl ion could be accomplished at a much lower cost. Moreover, it is known that calixarenes and their synergistic mixtures exhibit acceptable extracting behavior in the almost neutral pH ranges [9] in which it is difficult to maintain the pH of the source phase due to the hydrolysis and precipitation of uranyl ion. It is also worth mentioning that our recent uranyl ion transport system, based on the use of HBTA as a membrane carrier [13], was also suffering from such pH problem, although in the previous case the transport efficiency of HBTA was much higher than that of HTTA alone, reported in this work.

Based on our own experience [13] and some previous reports [2,3,9,14], in the present work we also expected the uranyl ion transport to be proton driven, so that the transfer of uranium(VI) from the source phase (at pH 2) to the receiving phase should be completed, at a proper length of time, by setting up a hydrogen-ion concentration gradient between the two sides of the membrane using a mineral acid with a relatively high concentration in the receiving phase. Thus, some preliminary transport experiments were carried out in the presence of 1.0 M solutions of hydrochloric, nitric, sulfuric and perchloric acids, and the results after 9 h transport showed the following order for transport of uranyl ion into receiving phase: HCl (72.1%) > H_2SO_4 (66.7%) > HNO_3 (54.7%) > $HClO_4$ (50.0%). As seen, in none of the acid systems exam-